

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
29 July 2004 (29.07.2004)

PCT

(10) International Publication Number
WO 2004/063126 A1

(51) International Patent Classification⁷: C05B 7/00, 9/00, 21/00

(21) International Application Number:
PCT/IL2004/000041

(22) International Filing Date: 15 January 2004 (15.01.2004)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
154007 16 January 2003 (16.01.2003) IL

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(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— with international search report

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WO 2004/063126 A1

(54) Title: SOLUBLE FERTILIZER COMPOSITIONS COMPRISING CALCIUM AND/OR MAGNESIUM PHOSPHATES

(57) Abstract: The present invention provides fertilizer compositions comprising calcium and magnesium phosphates together with alkali metal double phosphates, and process for their preparation. The solid composition is freely flowing and well soluble

-1- JC20 Rec'd PCT/PTO 11 JUL 2005

**SOLUBLE FERTILIZER COMPOSITIONS COMPRISING CALCIUM AND/OR
MAGNESIUM PHOSPHATES**

Field of the Invention

- 5 The present invention relates to solid, highly soluble fertilizer compositions, comprising Monobasic Calcium Phosphate (MCP) and/or Monobasic Magnesium Phosphate (MMgP), together with alkali metal double phosphates, which compositions are solid, freely flowing and highly soluble, and to a method for preparing said compositions.

10 **Background of the Invention**

- Monobasic Calcium Phosphate (MCP) $\text{Ca}(\text{H}_2\text{PO}_4)_2$ and Monobasic Magnesium Phosphate (MMgP) $\text{Mg}(\text{H}_2\text{PO}_4)_2$ are widely used as fertilizers. They have the drawback of being only slightly soluble in water, whereas such fertilizers are usually applied in aqueous solutions. However, solubility, while essential, is not the only property required.
- 15 Fertilizers must be packed, shipped and handled, and therefore must have appropriate physical properties, viz. must be adapted to form granules or powders that are free flowing, have low hygroscopicity, do not tend to agglomerate, and so forth. The art does not provide such fertilizers or their formulations having such optimal physical characteristics, in addition to high solubility.

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It is therefore the purpose of this invention to provide compositions, comprising MCP and/or MMgP, that have such desirable physical properties.

- It is another purpose of this invention to provide such compositions that are suitable for
- 25 use as components of food and/or drinks.

It is a further purpose to obtain such compositions in crystalline and homogeneous form.

- It is a further purpose to obtain such compositions which contain other fertilizer
- 30 compounds, preferably potassium compounds.

It is a further purpose to provide formulations from which such compositions are obtained and a process for obtaining said compositions from said formulations.

Summary of the Invention

The present invention, in one of its aspects, provides fertilizers formulations comprising the following components: 1) at least one monobasic earth-alkali metal phosphate, chosen from among Calcium Phosphate (MCP) $\text{Ca}(\text{H}_2\text{PO}_4)_2$, Magnesium Phosphate (MMgP) $\text{Mg}(\text{H}_2\text{PO}_4)_2$, or mixtures thereof; 2) at least one alkali metal phosphate; and 3) Phosphoric Acid (PA) H_3PO_4 . The alkali metal phosphate will be generally indicated hereinafter by MALP, and is preferably Monopotassium Phosphate (MKP) KH_2PO_4 . The term "alkali metal", as used herein, should be construed as including NH_4 .

10

The said formulations, as such, are an object of the invention. However, also according to the invention, they are subjected to a homogenizing, drying and heating processing, from which are obtained fertilizer compositions that can be stored, shipped and used for making aqueous solutions, said solution being applied to the areas to be fertilized. During the processing the alkali metal phosphate MALP reacts with PA to form a double salt, that will be indicated as $\text{AH}_5(\text{PO}_4)_2$ or, shortly, HAP, and is $\text{KH}_5(\text{PO}_4)_2$ if the alkali metal is potassium. In order to distinguish from the original mixture, which contains an alkali metal phosphate MALP and H_3PO_4 , and the processed material, which contains the double salt HAP and, optionally, an amount of MALP, the original mixture will be called hereinafter "fertilizer formulation" and the processed material will be called hereinafter "fertilizer composition".

15

The required amounts of the above components in the formulations are given hereinafter. Said amounts must satisfy the following conditions:

25

a) MALP (preferably MKP) is in a molar ratio to PA that is at least the ratio corresponding to the alkali metal double salt $\text{AH}_5(\text{PO}_4)_2$ (HAP). However, there may be a moderate excess of MALP over said ratio, viz. the ratio $\text{A}_2\text{O}:\text{P}_2\text{O}_5$ (preferably $\text{K}_2\text{O}:\text{P}_2\text{O}_5$), wherein the P_2O_5 does not comprise that included in phosphate moieties of the earth-alkali metal phosphates, must be from about 0.5 to about 0.8. Small departures from said limits may also be acceptable.

30

b) The molar ratio of CaO and/or MgO to $\text{P}_2\text{O}_5\text{T}$, wherein $\text{P}_2\text{O}_5\text{T}$ comprises the total amount of P_2O_5 included in the formulations, is: A) from 1:4.5 to 1:15.1, typically

1:4.8, if the earth-alkali metal is calcium; B) from 1:3.3 to 1:7.5, typically 1:3.8, if the earth-alkali metal is magnesium.

5 The compositions, after processing, comprise therefore MCP or MMgP and HAP, and may comprise an amount of MALP. The molar ratios of said components depend on the molar ratios of the formulations from which they derive. The molar ratio of CaO and/or MgO to P_2O_5 is the same as in the corresponding formulation. The molar ratio of MALP to HAP is from zero to 60%. Small departures from said limits may also be acceptable. Of course, additional components may be present to supply additional fertilizer moieties
10 or for other purposes known in the fertilizer art.

Another aspect of the invention is a process for the preparation of the compositions of the invention from the corresponding formulations. Said process comprises the steps of preparing the formulation, preferably in the form of a watery paste; introducing said
15 formulation into an drying oven of a material resistant to said components (particularly to the PA); and mechanically homogenizing the mixture, while concurrently drying it by heating under a vacuum.

If it is intended to use the product in food or drink, all the components must be of a
20 quality certified for such a use.

The compositions can be dissolved in water at room temperature or above it, and form clear solutions. Their solubility varies from 10 to 40 % by weight, the higher solubilities being attained when the earth-alkali metal is magnesium. Solutions of 1 wt% of the
25 above compositions have pH $2 \div 2.5$.

The properties of the compositions in their solid, dry state are as follows: grain size of their granulates or powders $0.05 < \text{diameter} < 1.0$ mm; bulk density of the $0.5 \div 1.2$; hygroscopicity $50 \div 70\%$ C.R.H. (critical relative humidity); free flowability index,
30 determined as described below, 40-70%.

The free flowing index is determined as follows. A funnel of stainless steel is used, having a smooth surface, a top diameter of 100 mm and a bottom diameter of 10 mm.

300 grams of the substance under examination are introduced into said funnel while keeping its bottom opening closed. Then the bottom opening is opened, the substance is allowed to flow into a receiving container, and the time required for it to flow completely through the funnel is measured. The same measurement is carried out for a substance used as standard. The flowability index FI% is $FI\% = 100(t_0/t_1)$, wherein t_0 is the flow time measured for the standard substance and t_1 is the flow time measured for the substance under examination. In this application, the standard substance is MKP and t_0 is 16 seconds. It is clear that the more quickly the substance under examination flows, the higher is its flowability index.

10

The compositions of the invention are crystalline. X-ray analysis shows two types of crystals: those of earth-alkali metal monophosphates $Ca(H_2PO_4)_2$ and/or $Mg(H_2PO_4)_2$ and crystals of AH_2PO_4 and $AH_5(PO_4)_2$, where A is the alkali metal.

15

The formulations can be ground, sieved and packed, e.g., in bags, for storage, transportation and selling to users, and they give clear aqueous solutions even close to or at saturation concentration.

Detailed Description of Preferred Examples

Ranges of optimal concentration ratios are given in Table I.

20

Table I

Optimal Ranges		Broad Ranges		Salt
CaO(MgO): A ₂ O	CaO(MgO): P ₂ O ₅ T	CaO(MgO): A ₂ O	CaO(MgO): P ₂ O ₅ T	
0.35 ÷ 0.66	0.14 ÷ 0.21	0.062 ÷ 0.74	0.032 ÷ 0.224	Ca(H ₂ PO ₄)
0.56 ÷ 1.76	0.19 ÷ 0.33	0.13 ÷ 2.12	0.075 ÷ 0.35	Mg(H ₂ PO ₄)

where A is either K, Na or NH₄.

25

In the Table P₂O₅T means total phosphoric anhydride, viz. the total amount of the P₂O₅ in the composition, comprising that which is part of the earth-alkali phosphates, the alkali phosphates and the phosphoric acid.

The following examples illustrate embodiments of the invention. The percentages are by weight.

5 **Example 1**

Into a drying oven, made of stainless steel and with a work volume of 6 liters, and provided with an agitator, the following chemicals were charged:

Phosphoric acid (P_2O_5 67.5%) 3123.8 gr

MKP (KH_2PO_4) 1824 gr

10 Slurry of Magnesium hydroxide ($Mg(OH)_2$ 79.5%) 879.3 gr, and 1219 gr of water (35% solids).

During the charge of those chemicals, the agitator was operated at 50 rpm. Once the charge was completed, heating was begun by means of a heating jacket with circulation of hot oil having a temperature of 120°C. Subsequently a vacuum pump was actuated,
15 gradually to avoid loss of material due to violent boiling since the vacuum may reach 50 mbar. Water was removed during two hours until the water content of the drier content was lowered to 0.36%. A powdery material is thus obtained, which is free-flowing and may be extracted and transferred to a storage vessel. A portion thereof remains in the oven, sticking to the agitator and the walls. The extracted powdery material has the
20 granulometry shown in the following table, in which the first column indicates the weight percentage of the fractions the size range of which is indicated in the second column in millimeters.

	26.9	>4 mm
	26.0	2-4 mm
25	20.3	1-2 mm
	14.4	0.45-1 mm
	4.9	0.25-0.45 mm
	5.3	0.125-0.25 mm
	2	<0.125 mm

30 The chemical analysis of the product indicates the following weight percentages:

P_2O_5 59.6%, K_2O 11.3%, MgO 8.8%. Turbidity NTU 4.

The product further contains the following metals:

<10 ppm heavy metals

- 10 ppm Zn
 0.4 ppm Pb
 0.46 ppm V
 1.3 ppm Mn
 5 13 ppm Fe
 1 ppm Cu
 0.2 ppm Cd
 1.3 ppm As
 The pH is 2.4
 10 Flowability Test – 64%
 Solubility at 20°C – 55%

Example 2

The drying oven used is the same as in Example 1. The materials charged into it are:

- 15 Phosphoric acid (P_2O_5 66.9%) 2239 gr
 MKP (KH_2PO_4) (99.8%) 1330.8 gr

Slurry containing 488 gr of $Ca(OH)_2$ dry, and 905.7 gr of water.

- During the charge of those chemicals, the agitator was operated at 50 rpm. Once the charge was completed, heating was begun by means of a heating jacket with circulation
 20 of hot oil having a temperature of 120°C. Subsequently a vacuum pump was actuated, gradually to avoid loss of material due to violent boiling since the vacuum may reach 50 mbar. Water was removed during two hours until the water content of the drier content was lowered to 1.5%. A powdery material is thus obtained, which is free-flowing and may be extracted and transferred to a storage vessel. A portion thereof remains in the
 25 oven, sticking to the agitator and the walls. The extracted powdery material has the granulometry shown in the following table, in which the first column indicates the weight percentage of the fractions the size range of which is indicated in the second column in millimeters.

- | | |
|--------|---------------|
| 7.7 | > 1 mm |
| 30 6.8 | 0.425-1 mm |
| 2.1 | 0.25-0.425 mm |
| 2.3 | 0.125-0.25 mm |
| 81.1 | < 0.125 mm |

The chemical analysis of the product indicates the following weight percentages: P_2O_5 % 57.1%, K_2O % 11.4%, CaO 8.5%. Turbidity NTU 18. Flowability Test – 70%. Solubility at 20°C – 41.7%. C.R.H. – 70%.

The pH is 2.5.

5

The product further contains the following metals:

10 ppm heavy metals

36 ppm Zn

0.26 ppm Pb

10 1.2 ppm V

2 ppm Mn

28 ppm Fe

1.3 ppm Cu

0.2 ppm Cd

15 0 ppm As

Example 3

The drying oven used is the same as in Example 1. The materials charged into it are:

Phosphoric acid (P_2O_5 67.5%) 4733.1 gr

20 Sodium hydroxide (NaOH 47.7%) 1363.5 g

Slurry containing 878.75 gr of $Mg(OH)_2$ (79.5%) and 1117 gr of water.

During the charge of those chemicals, the agitator was operated at 50 rpm. Once the charge was completed, heating was begun by means of a heating jacket with circulation of hot oil having a temperature of 120°C. Subsequently a vacuum pump was actuated,

25 gradually to avoid loss of material due to violent boiling since the vacuum may reach 50

mbar. Water was removed during two hours until the water content of the drier content

was lowered to 1.1%. A powdery material is thus obtained, which is free-flowing and may be extracted and transferred to a storage vessel. A portion thereof remains in the

oven, sticking to the agitator and the walls. The extracted powdery material has the

30 granulometry shown in the following table, in which the first column indicates the

weight percentage of the fractions the size range of which is indicated in the second column in millimeters.

13.1 >1 mm

13.2	0.425-1 mm
3.9	0.25-0.425 mm
18.7	0.125-0.25 mm
51.1	<0.125 mm

- 5 The chemical analysis of the product indicates the following weight percentages: P_2O_5 % 60.9%, Na_2O % 9.4%, MgO % 9.1%. Turbidity NTU 4.

The pH is 3.0.

The product further contains the following metals:

10 ppm heavy metals

10	21 ppm	Zn
	0.9 ppm	V
	1.7 ppm	Mn
	22 ppm	Fe
	0.32 ppm	Pb
15	0.9 ppm	Cu
	0.2 ppm	Ca
	0 ppm	As

Flowability – 42.1%. Solubility at 20°C – 51.9%.C.R.H. – 55%.

- 20 The above examples are intended to illustrate the invention and it is to be understood that the invention can be carried out with many modifications, adaptations and variations, without departing from its spirit or exceeding the scope of the claims.

CLAIMS

1. Fertilizer formulations comprising:
 - I) a monobasic earth-alkali metal phosphate, chosen from among Calcium Phosphate (MCP) $\text{Ca}(\text{H}_2\text{PO}_4)_2$, Magnesium Phosphate (MMgP) $\text{Mg}(\text{H}_2\text{PO}_4)_2$, or mixtures thereof;
 - II) an alkali metal phosphate (MALP) AH_2PO_4 ;
 - III) Phosphoric Acid (PA) H_3PO_4 .
2. Fertilizer formulations according to claim 1, wherein the alkali metal phosphate MALP is Monopotassium Phosphate (MKP) KH_2PO_4 .
3. Fertilizer formulations according to claim 1 or 2, wherein a) the alkali metal phosphate MALP is in a molar ratio to PA that is at least the ratio corresponding to the double salt $\text{AH}_5(\text{PO}_4)_2$.
4. Fertilizer formulations according to claim 1, wherein the ratio $\text{A}_2\text{O}:\text{P}_2\text{O}_5$, wherein the P_2O_5 does not comprise that included in phosphate moieties of the earth-alkali metal phosphates, is from about 0.50 to about 0.80.
5. Fertilizer formulations according to claim 1, wherein the molar ratio CaO and/or MgO to $\text{P}_2\text{O}_5\text{T}$, wherein $\text{P}_2\text{O}_5\text{T}$ comprises the total amount included in the formulations, is from 1:4.5 to 1:15.1 if the earth-alkali metal is calcium, and from 1:3.3 to 1:7.5, if the earth-alkali metal is magnesium.
6. Fertilizer formulations according to claim 5, wherein the molar ratio CaO and/or MgO to $\text{P}_2\text{O}_5\text{T}$, wherein the $\text{P}_2\text{O}_5\text{T}$ comprises the total amount included in the formulations, is about 1:4.8 if the earth-alkali metal is calcium, and about 1:3.8, if the earth-alkali metal is magnesium.
7. Fertilizer compositions comprising:

a monobasic earth-alkali metal phosphate, chosen from among Calcium Phosphate (MCP) $\text{Ca}(\text{H}_2\text{PO}_4)_2$, Magnesium Phosphate (MMgP) $\text{Mg}(\text{H}_2\text{PO}_4)_2$, or mixtures thereof, and an alkali metal double salt $\text{AH}_5(\text{PO}_4)_2$, wherein $\text{A}=\text{K}, \text{Na}, \text{NH}_4$.

8. Fertilizer compositions according to claim 7, further comprising an alkali metal phosphate (MALP) AH_2PO_4 .

9. Fertilizer compositions according to claim 7, wherein the alkali metal double salt is $\text{KH}_5(\text{PO}_4)_2$.

10. Fertilizer compositions according to claim 8, wherein the alkali metal phosphate MALP is Monopotassium Phosphate (MKP) KH_2PO_4 .

11. Fertilizer compositions according to claim 7, 8 or 9, wherein the molar ratio of CaO and/or MgO to $\text{P}_2\text{O}_5\text{T}$, wherein the $\text{P}_2\text{O}_5\text{T}$ comprises the total amount included in the compositions, is from 1:4.5 to 1:15.1 if the earth-alkali metal is calcium, and from 1:3.3 to 1:7.5, if the earth-alkali metal is magnesium.

12. Fertilizer compositions according to claim 11, wherein the molar ratio CaO and/or MgO to $\text{P}_2\text{O}_5\text{T}$, wherein the $\text{P}_2\text{O}_5\text{T}$ comprises the total amount included in the compositions, is about 1:4.8 if the earth-alkali metal is calcium, and is about 1:3.8, if the earth-alkali metal is magnesium.

13. Fertilizer compositions according to claim 11, wherein the molar ratio of MALP to $\text{AH}_5(\text{PO}_4)_2$ is from zero to 60%.

14. Process for the preparation of the compositions of the invention, which comprises the steps of preparing a formulation according to any one of claims 1 to 6; introducing said formulation into a drying oven of a material resistant to the components of said formulation (particularly to the PA); and mechanically homogenizing said formulation while concurrently drying it by heating under a vacuum.

Abstract

The present invention provides fertilizer compositions comprising calcium and magnesium phosphates together with alkali metal double phosphates, and process for their preparation. The solid composition is freely flowing and well soluble

INTERNATIONAL SEARCH REPORT

International Application No
PCT/IL2004/000041

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C05B7/00 C05B9/00 C05B21/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C05B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DE 19 22 968 A (MUELLER DR DIPL CHEM FRANZ) 19 November 1970 (1970-11-19) the whole document	1-14
A	DE 19 25 180 A (MUELLER DR DIPL CHEM FRANK) 26 November 1970 (1970-11-26) the whole document	1-14
A	DE 19 24 284 A (MUELLER DR FRANK) 19 November 1970 (1970-11-19) the whole document	1-14

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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- "A" document defining the general state of the art which is not considered to be of particular relevance
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Date of the actual completion of the international search

5 May 2004

Date of mailing of the international search report

13/05/2004

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INTERNATIONAL SEARCH REPORT

Information on patent family members

Int. Patent Application No
PCT/IL2004/000041

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
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